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Synthesis and characterization of luminescent copolyethers with alternate stilbene derivatives and aromatic 1,3,4-oxadiazoles

Yun Chen*, Chi-Kuei Liao, Tzi-Yi Wu

Department of Chemical Engineering, National Cheng-Kung University, Tainan 701, Taiwan, ROC

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Abstract

New copoly(aryl ether)s containing alternate stilbene (**P1**), distyrylbenzene (**P2**), or distyrylstilbene (**P3**) chromophores and aromatic 1,3,4-oxadiazole were prepared by nucleophilic polycondensation. The copolyethers are basically amorphous materials with decomposition temperature greater than 250 °C. Introduction of side hexyloxy groups to distyrylbenzene chromophores in **P2** significantly enhanced its solubility in common organic solvents such as toluene, THF, and chloroform. UV/visible and fluorescence spectrometers were employed to investigate their optical properties both in solution and in film state, whereas cyclic voltammograms were used to estimate their band diagrams. Photoluminescence maxima of **P1**, **P2** and **P3** are 442, 540 and 528 nm, respectively. Oxadiazole chromophores in backbone enhance electron affinity, whereas pendant hexyloxy groups decrease ionization potential. The threshold voltage and luminance of ITO/**P2** (100 nm)/Al single layer device are 17 V and 950 cd/m^2, respectively. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Oxadiazole; Photoluminescence; Electrochemical property

1. Introduction

Since the first emitting conjugated poly(*p*-phenylene vinylene) (PPV) reported by Cavendish Laboratory of Cambridge university in 1990, the researches on electroluminescent polymers for organic light emitting diodes (OLED) have been expanded greatly [1,2]. The conjugated polymers have excellent advantages for low cost, large-area flat-panel displays because of their unique process ability, band gap tunability, and mechanical flexibility. Many con jugated polymers, such as PPV, poly(*p*-phenylene)s (PPPs) [3,4], polyfluorenes (PFs) [5], and polythiophenes (PTs) [6,7] have been synthesized for tentative application as emissive layers in OLEDs. However, some problems such as luminescent efficiency and long-term stability remain to be resolved.

The emissive light of OLEDs arises from the recombination of electrons and holes, which are injected from the two opposite electrodes, to become excitons in an emissive polymer layer. To achieve high electroluminescence efficiency, it is necessary to balance the rates of injection of electrons and holes from the opposite contacts into the polymer layer [8]. In general, the conjugated polymers, such as PPVs, PPPs, PFs, and PTs, have better hole efficiency due to the low ionization potential (high HOMO). This makes imbalance of injection rate between electrons and holes. To overcome this problem, one approach is to use metals with low work function (such as Ca and Mg) as cathode materials [9]. Such metals, however, are so highly susceptible to atmospheric degradation and are difficult to encapsulate that the resulting devices suffer from poor stability. The other approach is to insert an additional electron-transporting layer between the emissive layer and cathode [10]. Although this have been proven to be an effective way of achieving improved efficiency, the fabrication of multilayer devices is tedious and requires careful selection of each layer so that the solution of a subsequent layer will not attack the previous one. How to fabricate a single layer device with high efficiency and various colors has been attempted recently. Many conjugated polymers containing electron-transporting chromophores have been synthesized to overcome these problems about work function and balance of injection [11–13]. However, excess conjugated length usually results in red-shifting the wavelength of photoluminescence (PL) or electroluminescence [14]. Moreover, the defects in main chain may become the trap of excitons that leads to decreased efficiency. Isolated emitting and electron-transporting chromophores seems potential in improving color purity and PL efficiency [15–17].

We have been preparing copolyethers with isolated

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* Corresponding author.
E-mail address: yunchen@mail.ncku.edu.tw (Y. Chen).

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emitting and electron-transporting groups and investigating their optical and electrochemical properties [18–22]. In the work, three new copolyethers with stilbene, distyrylbenzene, or distyrylstilbene derivatives and aromatic 1,3,4-oxadiazole chromophores have been synthesized by nucleophilic polycondensation. Their preparation, characterization, optical and electrochemical properties are presented.

2. Experimental section

2.1. Materials and measurements

Reagent chemicals were purchased from Aldrich, Lancaster, TCI, and Acros Chemical Co. All new compounds were characterized using ^{1}H NMR, FT-IR, and elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker 400 MHz FT-NMR and chemical shifts were reported in δ ppm using tetramethylsilane (TMS) as internal standard. Infrared spectra were measured as KBr pellets on a Fourier transform infrared spectrometer, model Valor III from Jasco. Elemental analyses were carried out on a Heraus CHN-Rapid elemental analyzer. Thermal properties of the polymers were measured using a differential scanning calorimetry (DSC), Perkin Elmer DSC 7, under nitrogen atmosphere at a heating rate of 20 °C/min. The thermogravimetric analyses (TGA) of the polymers were measured under nitrogen atmosphere at a heating rate of 20 °C/min using a Perkin Elmer TGA-7 thermal analyzer. The UV/visible spectra were measured using a Jasco V-550 spectrophotometer. The PL spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer, excited with 365 nm light from a 150 W Xenon lamp. The cyclic voltammograms (CV) of polymer films were measured at room temperature under nitrogen atmosphere using polymer-coated ITO glass as working electrode, Ag/AgCl electrode as reference electrode, and platinum wire electrode as auxiliary electrode supporting in $(n\text{-Bu})_4NClO_4$/acetonitrile solvent, the scanning speed was 100 mV/s.

2.2. Synthesis of difluoride monomer **7** (Scheme 1)

2.2.1. 2,5-Bishexyloxyterephthalic acid diethyl ester (**3**)

To a two-necked glass reactor was added diethyl-2-5-dihydroxyterephthalate (**1**: 0.51 g, 2 mmol), potassium carbonate (0.576 g, 4.16 mmol) and 7 ml DMF. The mixture was added with **2** (0.763 g, 4.1 mmol) after purging with nitrogen and heated to 80 °C to react for 30 h. It was poured into 100 ml water and then extracted with chloroform (50 ml × 3). The solids after drying were recrystallized from methanol to obtain white powders of **3** (Yield: 67.2%, mp: 64–65 °C). IR (KBr, pellet): ν 2952 (C–H), 2861, 1695, 1417, 1386, 1300, 1211 (–C–O–C–), 1024 cm^{-1}. ^{1}H NMR (acetone-d$_6$, ppm): δ 0.84–0.87 (m, 6H, $-CH_3$), 1.26–1.69 (m, 22H, $-CH_2-$ and $-CH_3$), 3.94–3.97 (m, 4H, $-OCH_2-$), 4.23–4.28 (m, 4H, $-OCH_2-$), 7.26 ppm (s, 2H, aromatic). Anal. Calcd (%) for $C_{24}H_{38}O_6$: C, 68.18; H, 9.07. Found: C, 68.22; H, 9.06.

2.2.2. 2,5-Bishexyloxyterephthalic dihydrazide (**4**)

2,5-Bishexyloxyterephthalic acid diethyl ester (**3**: 0.844 g, 2 mmol) and hydrazine monohydrate (1.4 ml) were added into 8 ml ethanol (99.5%), and the mixture was stirred at 78 °C for 24 h. The appearing solids after pouring into 150 ml water were collected by filtration and dried completely. Recrystallization from 95% ethanol resulted in white cotton-like products of **4** (Yield: 75.7%, mp: 114–115 °C). IR (KBr, pellet): ν 3385, 3309 (–NH–), 3219, 2919 (C–H), 2850, 1624 (–C=O), 1460, 1383, 1202, 1022, 971, 804, 589 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, ppm): δ 0.84–0.88 (m, 6H, $-CH_3$), 1.29–1.76 (m, 16H, $-CH_2-$), 4.02–4.06 (m, 4H, $-OCH_2-$), 7.37 ppm (s, 2H, aromatic). Anal. Calcd (%) for $C_{20}H_{34}N_4O_4$: C, 60.87; H, 8.70; N, 14.10. Found: C, 60.89; H, 8.69; N, 14.20.

2.2.3. Difluoro-bis(hydrazide) (**6**)

4-Fluorobenzoyl chloride (**5**: 0.405 g, 2.08 mmol), 2,5-bishexyloxyterephthalic dihydrazide (**4**: 0.401 g, 1 mmol), and 3 drops pyridine were dissolved in 5 ml NMP, and the mixture was stirred at room temperature for 4 h. The solids appeared at pouring into 200 ml water were collected by filtration and dried completely. Recrystallization from chloroform led to white powders of **6** (Yield: 63.9%, mp: 283–284 °C). IR (KBr, pellet): ν 3192 (–NH–), 2951 (C–H), 1604 (–C=O), 1580, 1471, 1210, 1160, 850, 752 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, ppm): δ 0.86–0.88 (m, 6H, $-CH_3$), 1.15–1.84 (m, 16H, $-CH_2-$), 4.14–4.18 (t, 4H, $-OCH_2-$), 7.31–8.03 ppm (m, 10H, aromatic). Anal. Calcd (%) for $C_{34}H_{40}N_4O_6$: C, 63.63; H, 6.37; N, 8.96. Found: C, 63.94; H, 6.31; N, 8.77.

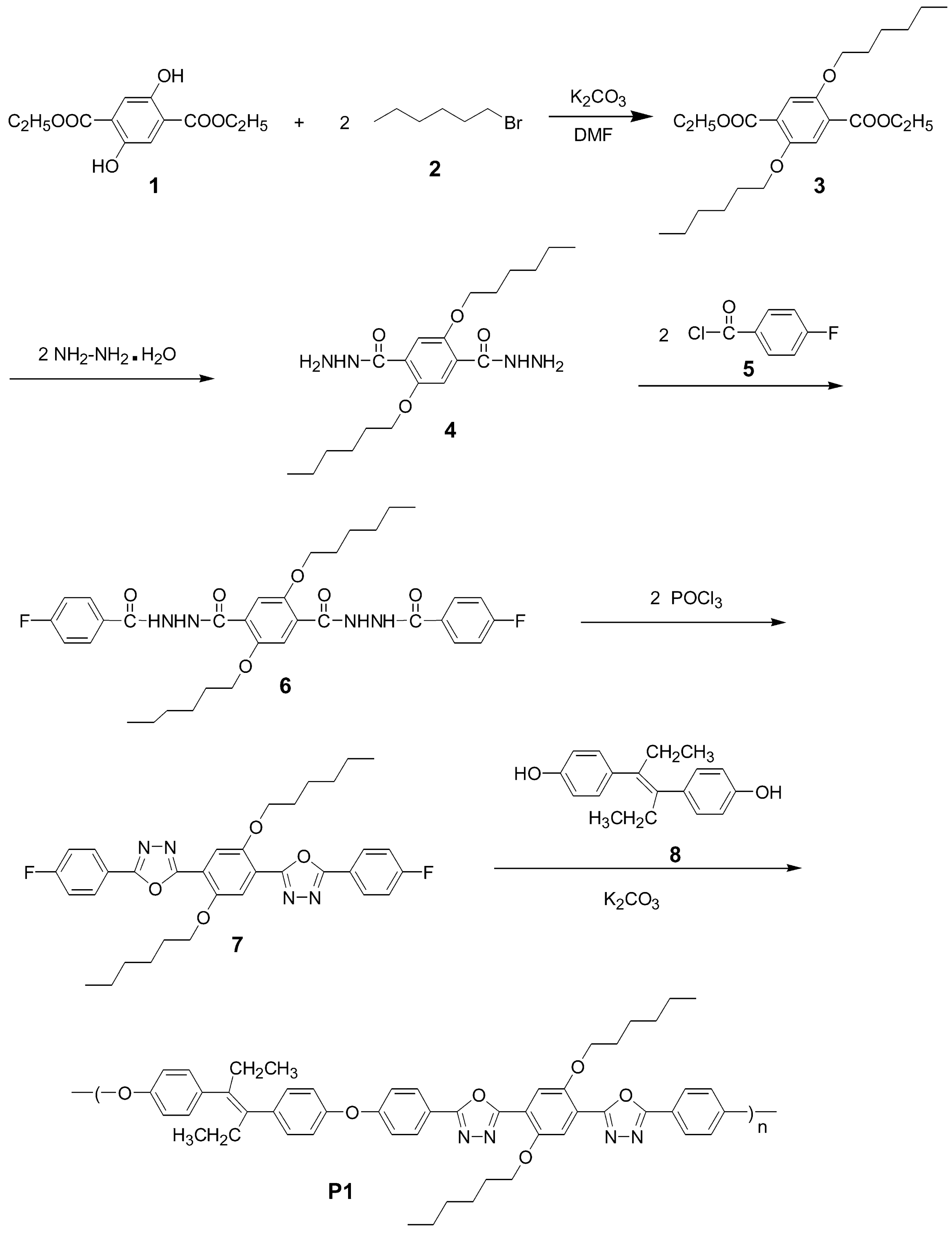
2.2.4. 5,5′-Di-(4-fluorophenyl)-2,2′-p-(2,5-bishexyloxyphenylene)-bis-1,3,4-oxadiazole (**7**)

Compound **6** (0.320 g, 0.5 mmol) was dissolved in 4 ml $POCl_3$ and stirred at 110 °C for 12 h. The mixture was poured into 150 ml water and the appearing solids were collected by filtration and dried completely. Recrystallization from benzene resulted in light green cotton-like products of **7** (Yield: 68.5%, mp: 181–182 °C). IR (KBr, pellet): ν 2935 (C–H), 2862, 1609 (–C=N–), 1495, 1445, 1222, 1156, 843, 748 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, ppm): δ 0.78–0.83 (m, 6H, $-CH_3$), 1.23–1.83 (m, 16H, $-CH_2-$), 4.18–4.23 (m, 4H, $-OCH_2-$), 7.43–8.17 ppm (m, 10H, aromatic). Anal. Calcd (%) for $C_{34}H_{36}F_2N_4O_4$: C, 67.75; H, 6.04; N, 9.32. Found: C, 67.76; H, 6.02; N, 9.30.

2.3. Synthesis of diphosphonate monomers (**12, 19**) (Schemes 2 and 3)

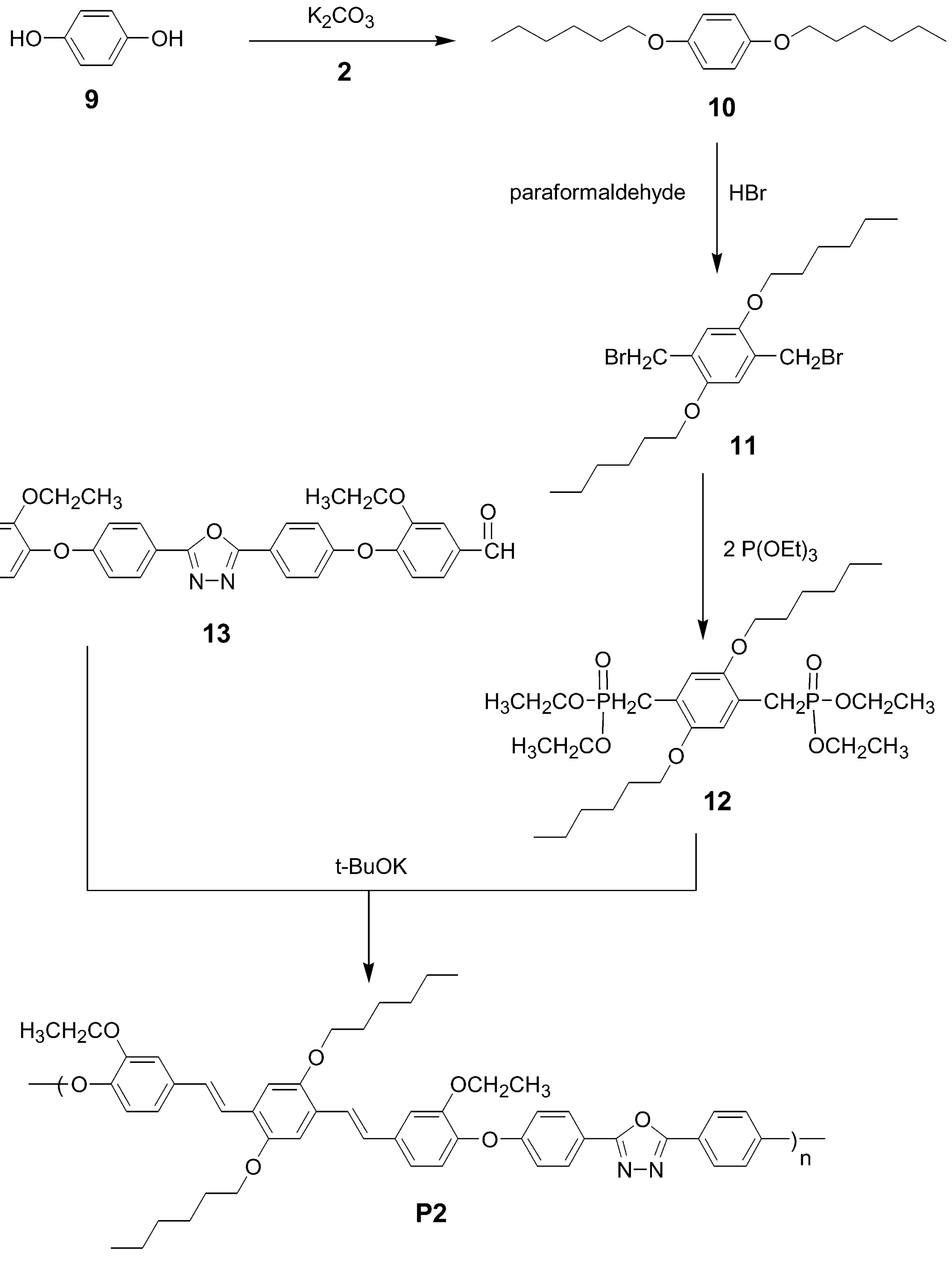
2.3.1. 1,4-Bishexyloxybenzene (**10**)

To a two-necked 50-ml glass reactor were added hydroquinone (**9**: 0.56 g, 5 mmol), 1-bromohexane (**2**:



Scheme 1.

1.695 g, 10.1 mmol), potassium carbonate (1.496 g, 10.4 mmol) and 18 ml DMF. The solution was allowed to react at 100 °C for 24 h and then precipitated in 300 ml deionized water. The appearing violet–black solids were collected and recrystallized from methanol to give rise to light violet pellet crystals of **10** (Yield: 50.8%, mp: 57–58 °C). IR (KBr, pellet): ν 2936 (C–H), 2872, 1511, 1475, 1396, 1287, 1242, 1115, 1033, 996, 828, 772, 726, 534 cm^{-1}. ^{1}H NMR (acetone-d_6, ppm): δ 0.87–0.90 (m, 6H, $-CH_3$), 1.31–1.73 (m, 16H, $-CH_2-$), 3.88–3.91 (m, 4H, $-OCH_2-$), 6.82 ppm (s, 2H, aromatic). Anal. Calcd (%) for $C_{18}H_{30}O_2$: C, 77.67; H, 10.78. Found: C, 77.65; H, 10.86.



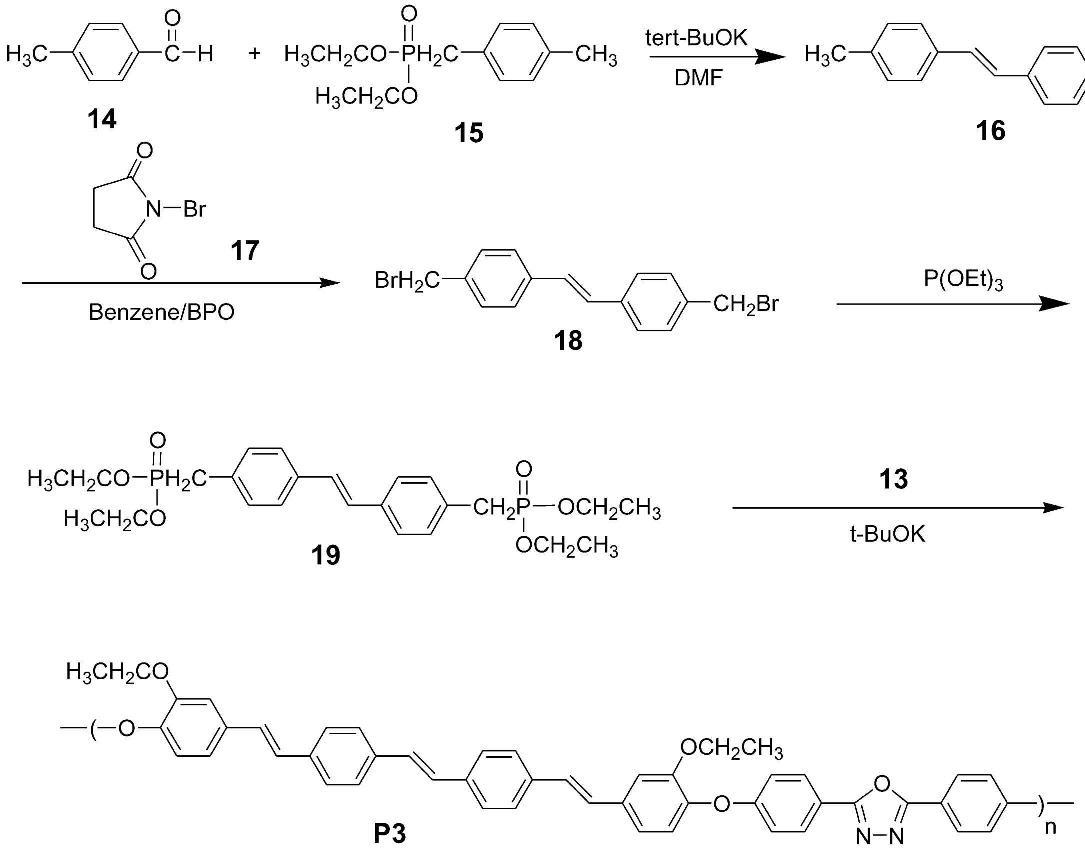
Scheme 2.

2.3.2. *1,4-Bisbromomethyl-2,5-bishexyloxybenzene (**11**)*

To a 25-ml two-necked reactor was added 1,4-bishexyloxybenzene (**10**: 1.398 g, 5 mmol), paraformaldehyde (0.63 g, 21 mmol) and HBr solution (1.869 g in 15 ml acetic acid, 23.1 mmol). The mixture was warmed up to 80 °C slowly and allowed to react for 24 h. The appearing white solids, after pouring into 100 ml water and neutralizing with saturated $NaHCO_3$ aqueous solution, were collected and recrystallized from *n*-hexane to obtain cotton-like crystals of **11** (Yield: 56.8%. mp: 90–91 °C). IR (KBr, pellet): ν 2942 (C–H), 2870, 1510, 1474, 1413, 1397, 1314, 1224, 1204, 1028, 864, 725, 690, 545 cm^{-1}. ^1H NMR (acetone-d_6, ppm): δ 0.87–0.92 (m, 6H, $-CH_3$), 1.33–1.85 (m, 16H, $-CH_2-$), 4.01–4.06 (m, 4H, $-OCH_2-$), 4.61 (s, 4H, $-CH_2Br$), 7.08 ppm (s, 2H, aromatic). Anal. Calcd (%) for $C_{30}H_{32}O_2Br_2$: C, 51.80; H, 6.97. Found: C, 51.74; H, 6.95.

2.3.3. *1,4-Bis(diethoxyphosphorylmethyl)-2,5-bishexyloxybenzene (**12**)*

The mixture containing **11** (0.464 g, 1 mmol) and 5 ml $P(OEt)_3$ was allowed to react at 150 °C for 3 h under nitrogen blanket. White products of **12** were obtained after removing excess $P(OEt)_3$ by vacuum distillation (Yield:



Scheme 3.

65.6%, mp: 56–57 °C). IR (KBr, pellet): ν 2953 (C–H), 1513, 1473, 1392, 1274, 1211, 1030, 947, 840, 641, 523 cm^{-1}. ^{1}H NMR (acetone-d$_6$, ppm): δ 0.88–0.91 (m, 6H, –CH_3), 1.17–2.05 (m, 24H, –CH_2– and –CH_3), 3.14–3.19 (s, 4H, –CH_2), 3.94–4.01 (m, 12H, –OCH_2–), 6.98 ppm (s, 2H, aromatic). Anal. Calcd (%) for $C_{28}H_{52}O_8P_2$: C, 58.05; H, 9.07. Found: C, 58.12; H, 9.06.

2.3.4. *4,4′-Dimethylstilbene (**16**)*

To a two-necked 25-ml glass reactor containing 12 ml DMF was added *t*-BuOK (0.882 g, 7.8 mmol) and diethyl 4-methylbenzylphosphonate (**15**: 1.472 g, 6 mmol) under nitrogen blanket. After stirring at ambient temperature for 1 h, the solution was added with *p*-tolualdehyde (**14**: 0.783 g, 6 mmol) dissolved in 6 ml DMF and allowed to react for another 24 h. The green solids, appeared at pouring the solution into 200 ml water, were collected and recrystallized from 95% ethanol to give cotton-like crystals of **16** (Yield: 50.2%, mp: 197–198 °C). IR (KBr, pellet): ν 3019, 1514, 971 (*trans* –C=C–), 822, 717, 531 cm^{-1}. ^{1}H NMR (acetone-d$_6$, ppm): δ 2.31 (s, 6H, –CH_3), 7.14–7.46 ppm (m, 10H, aromatic). Anal. Calcd (%) for $C_{16}H_{16}$: C, 92.25; H, 7.82. Found: C, 92.26; H, 7.74.

2.3.5. *4,4′-Dibromomethylstilbene (**18**)*

To a two-necked 50-ml reactor were added **16** (0.21 g, 1 mmol), *N*-bromosuccinimide (**17**: 0.38 g, 2.1 mmol) and 20 ml benzene. After purging with nitrogen for 30 min, the solution was added with benzoyl peroxide (0.015 g, 0.063 mmol) and allowed to react at 85 °C for 24 h. The solution was washed with de-ionized water (20 ml × 4) and vacuum dried using a rotavapor. The residual solids were recrystallized from ethyl acetate/*n*-hexane mixture solvent to obtain yellow crystals of **18** (30.2%, mp: 199–200 °C). IR (KBr, pellet): ν 1420, 1201, 967 (*trans* –C=C–), 838, 768, 604, 532 cm^{-1}. ^{1}H NMR (acetone-d$_6$, ppm): δ 4.66 (s, 4H, –CH_2Br), 7.29–7.61 ppm (m, 10H, aromatic). Anal. Calcd (%) for $C_{16}H_{14}Br_2$: C, 52.55; H, 3.85. Found: C, 52.49; H, 3.85.

2.3.6. *4,4′-Bis(diethoxyphosphorylmethyl)stilbene (**19**)*

To a two-necked 10-ml glass reactor were added **18** (0.367 g, 1 mmol) and 5 ml P(OEt)$_3$. The solution was stirred at 150 °C for 6 h under nitrogen atmosphere. The excess P(OEt)$_3$ was removed by vacuum distillation to obtain green solids of **19** (52.8%, 140–141 °C). IR (KBr, pellet): ν 2984, 1515, 1392, 1028, 966 (*trans* –C=C–), 869, 807, 571, 494 cm^{-1}. ^{1}H NMR (acetone-d$_6$, ppm): δ 1.14–1.17 (m, 12H, –CH_3), 3.12–3.24 (s, 4H, –CH_2–), 3.90–3.97 (m, 8H, –OCH_2–), 7.19–7.53 ppm (m, 10H, aromatic and vinylic). Anal. Calcd (%) for $C_{24}H_{34}O_6P_2$: C, 59.62; H, 7.18. Found: C, 59.89; H, 7.13.

2.4. Preparation of copolyethers (Schemes 1–3)

Polyethers **P1** was prepared by nucleophilic substitution of aromatic difluoride (**7**) with diethylstilbestrol (**8**) using potassium carbonate as catalyst. Monomer **7** (0.606 g, 1 mmol), diethylstilbestrol (0.270 g, 1 mmol), and K_2CO_3 (0.290 g, 2.1 mmol) were dissolved in 20 ml mixed solvent of toluene/NMP/*N*-cyclohexylpyrrolidone (CHP) (2:1:1 by volume). The mixture was first refluxed at 150 °C for 2 h to remove trace water through Dean–Stark trap and then stirred at 170 °C for 48 h. The appearing solids, at pouring into excess methanol/water (1:1), were collected and extracted with methanol overnight to obtain **P1** (0.8 g, Yield: 96.3%, η_{red}: 0.25 dl/g). IR (KBr, pellet): ν 2929 (C–H), 1599 (–C=N–), 1490, 1241 (–C–O–C), 1021, 873 cm^{-1}. ^1H NMR (acetone-d_6, ppm): δ 0.71–0.80 (m, 12H, $-CH_3$), 1.10–1.63 (m, 12H, $-CH_2-$), 1.84–2.14 (m, 8H, $-CH_2$), 4.11 (s, 4H, $-OCH_2-$), 6.97–8.10 ppm (m, 18H, aromatic).

Polyethers **P2** and **P3** were synthesized by condensing **12** and **19**, respectively, with dialdehyde monomer **13**, whose synthetic route was reported previously [22]. For example, to a two-necked 25-ml reactor was added 4 ml NMP and 5 ml toluene. The solution was heated to 160 °C to remove trace water by azeotropic distillation with toluene for 2 h. After cooling to ambient temperature, it was added with **12** (0.579 g, 1 mmol) and *t*-BuOK (0.234 g, 2.08 mmol) and allowed to react at 0 °C for 1 h under nitrogen blanket. Then dialdehyde monomer **13** was added and the reaction continued for another 90 h. The colors changed from original dark red to black green, and then to orange after 6 h. Pouring the solution into the mixture of methanol/water (1:10 by volume) precipitated orange products of **P2** (0.471 g, Yield: 57.4%, η_{red}: 0.22 dl/g). IR (KBr, pellet): ν 2928 (C–H), 1695, 1612 (–C=N–), 1488, 1268, 1225 (–C–O–C–), 1163, 1038, 960 cm^{-1} (*trans* –C=C–). ^1H NMR ($C_2D_2Cl_4$, ppm): δ 0.90–0.95 (m, 6H, $-CH_3$), 1.10–1.88 (m, 22H, $-CH_2-$ and $-CH_3$), 4.00–4.15 (m, 8H, $-CH_2$), 6.97–8.07 ppm (m, 20H, aromatic).

The **P3** was prepared by similar procedures, to a two-necked 25-ml reactor was added 4 ml NMP and 5 ml toluene. The solution was heated to 160 °C to remove trace water by azeotropic distillation with toluene for 2 h. After cooling to ambient temperature, it was added with **19** (0.481 g, 1 mmol) and *t*-BuOK (0.234 g, 2.08 mmol) and allowed to react at 0 °C for 1 h under nitrogen blanket. Then dialdehyde monomer **13** was added and stirred for another 96 h. Pouring the solution into the mixture of methanol/water (1:1 by volume) precipitated the products, which were extracted with acetone for 24 h using a Soxhlet extractor to give **P3** (0.586 g, Yield: 81.1%, η_{red}: 0.31 dl/g). IR (KBr, pellet): ν 1661 (–C=N–), 1487, 1223 (–C–O–C–), 1163, 957 (*trans* –C=C–), 830, 743 cm^{-1}. ^1H NMR ($CF_3COOD/CDCl_3$, ppm): δ 1.29–1.39 (m, 6H, $-CH_3$), 4.23–4.24 (m, 4H, $-OCH_2-$), 7.14–8.12 ppm (m, 28H, aromatic).

2.5. Fabrication of single layer EL device

Polymer solution (15 mg/ml in toluene) was first prepared and filtered with a syringe filter (0.22 μm pore size) to remove possible particle contamination. Single layer LED device of **P2** was fabricated by spin-coating polymer solution (15 mg/ml in toluene, 1000 rpm) onto ITO (25 Ω/square) glass substrate. Polymer film thickness was about 100 nm, as determined by scanning probe microscope (SPM). An aluminum cathode of about 100 nm thickness was vapor-deposited through a mask on top of the polymer film at 10^{-5} Torr of pressure.

3. Results and discussion

3.1. Preparation and solubility of the copolyethers

In general, PPV-based conjugated polymers were usually prepared by Wessling method [23]. However, their rigid main chain and significant intermolecular interaction lead to insolubility in organic solvents. The solubility can be improved by incorporating long side alkyl or alkoxy groups. For our copolyethers with alternate emitting and electron-transporting chromophores, two nucleophilic substitution routes were employed. First, **P1** was synthesized from aromatic difluoride (**7**) and diphenol (**8**) via polycondensation procedure as shown in Scheme 1. On the other hand, **P2** and **P3** were prepared by nucleophilic polycondensation of oxadiazole-containing dialdehyde (**13**) with diphosphonate (**12** or **19**), during which the emitting chromophores were formed as shown in Schemes 2 and 3. The polymerization can be traced by ^1H NMR spectra focusing on chemical shift of aldehyde proton near δ 10 ppm (Fig. 1). The peak decreased in intensity as polymerization proceeded. Infrared spectra showed similar peak transformation, i.e. aldehyde peak of **13** at 1703 cm^{-1} decreased drastically in intensity when converted to **P2**.

As depicted in Table 1, the viscosities of the copolyethers are between 0.22 and 0.31 dl/g and the yields are between 48 and 80%. The molar mass (M_n) and weight mass (M_w) of **P2**, measured by gel-permeation chromatography (GPC) using tetrahydrofuran as eluent and monodisperse polystyrene as standard, were 11,400 and 16,100, respectively. The polydispersity index was estimated to be 1.41. However, those of **P1** and **P3** could not be obtained due to limited solubility in THF. In order to elucidate the structure–property relationship for the copolyethers, the results of **O1** [18] and **O2** [22] prepared previously were also depicted in Table 1. Compared to **O1** structurally, **P1** possesses extra oxadiazole in backbone and hexyloxy group in side chain. Both **P2** and **O2** consist of alternate distyrylbenzene and aromatic 1,3,4-oxadiazole chromophores but **P2** possesses additional side hexyloxy groups in distyrylbenzene segment. However, **P3** consist of alternate distyrylstilbene and aromatic 1,3,4-oxadiazole.

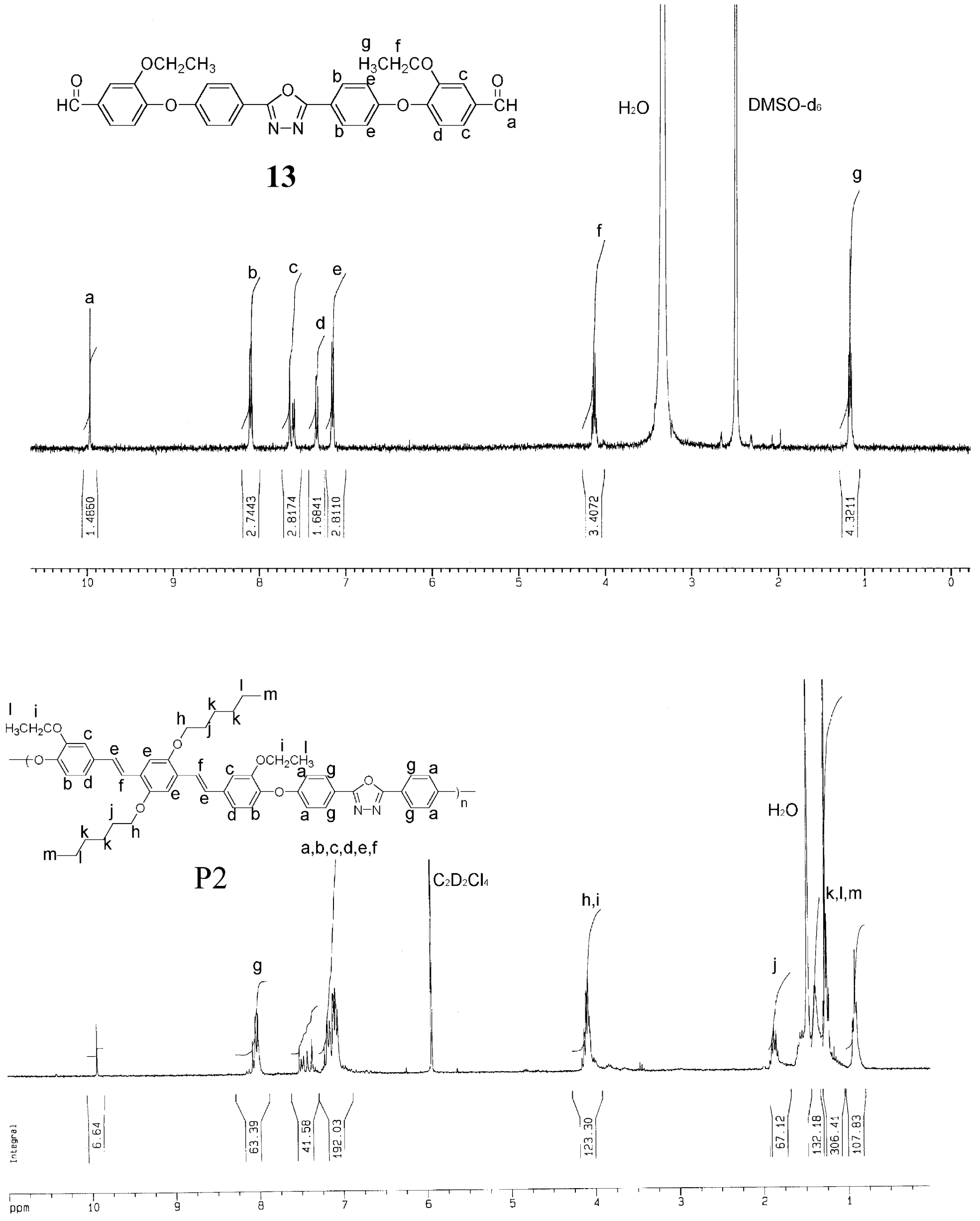


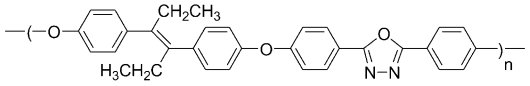
Fig. 1. ^{1}H NMR spectra of **13** and **P2**.

The **P1** contains extra oxadiazole in backbone and two hexyloxy in side group in its repeating unit as compared with **O1**. The solubility of **P1** is lower than **O1**, suggesting that extra oxadiazole in **P1** leads to decreased solubility regardless of added hexyloxy side groups. This is coincident with the rigid characteristics of aromatic oxadiazole, especially when linked in sequence. The **P2**, consisting of alternate oxadiazole and hexyloxy-substituted distyrylbenzene segments, is soluble in common organic solvents such as toluene, THF, and chloroform, whereas **O2** show solubility only in $CF_3COOH/CHCl_3$ (1:3 by volume) and NMP. For **P2** transparent and self-standing film can be cast using these solvents. However, the solubility of **P3** is also poor and soluble only in solvent mixture of CF_3COOH and $CHCl_3$ (1:3 by volume). This is ascribed to absence of side alkoxy groups and increased backbone rigidity due to extended conjugation.

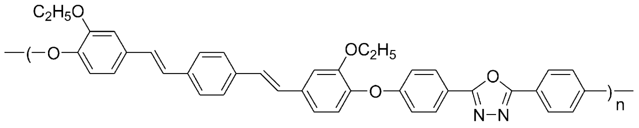
3.2. Thermal property of copolyethers

As shown in Fig. 2, thermal decompositions (T_ds) of **P1**, **P2** and **P3** (at 5% weight loss) under nitrogen flow are at 411, 387 and 250 °C, respectively, and significant decomposition starts at about 400 °C. The T_d of **P2** is much lower than that of **O2** ($T_d = 451$ °C) [22], suggesting that two hexyloxys in distyrylbenzene chromophore depress the heat resistance of **P2**. However, **P3** has a shorter side chain than **P1** and **P2** and should be slightly more stable than **P1** and **P2**. Therefore, first small weight loss at about 180 °C may be due to trace NMP solvent which is hard to remove during

Table 1
Yield, viscosity and solubility of the copolyethers



O1



O2

Polymer	Yield (%)	η_{red}[a] (dl/g)	Solubility in solvents[b]						
			$CF_3COOH/CHCl_3$	DMSO[c]	NMP	$CHCl_3$	$C_2H_2Cl_4$	THF	Toluene
P01	48	0.25	++	+ −	+ −	+ −	++	+ −	− −
O1	–	–	++	− −	++	++	++	++	++
P2	57.4	0.22[d]	++	++	++	++	++	++	++
O2	–	–	++	+	++	− −	+	− −	− −
P3	80.1	0.31[e]	++	+ −	+ −	+ −	+	+ −	+ −

[a] Reduced viscosity: measured at a concentration of 0.3 g/dl at 30 °C.

[b] Concentration: 1 mg/ml; ++: soluble at room temperature; +: soluble by heating; + − : partially soluble and/or swelling; − −: insoluble.

[c] DMSO: dimethyl sulfoxide; NMP: *N*-methyl-2-pyrrolidone; THF: tetrahydrofuran.

[d] Measured in $CHCl_3$.

[e] Measured in $CF_3COOH/CHCl_3 = 1:3$.

purification procedures. The residual weights at 800 °C are still very high (**P1**: 32.5%; **P2**: 37.9%; **P3**: 59.1%), suggesting that these polymers are readily carbonized or graphitized at elevated temperature. Glass transition temperature (T_g) of **P1** is 137 °C as determined from the DSC thermogram, but no phase transition could be observed up to 300 °C for **P2** and **P3**.

3.3. Optical property

The absorption spectra of the copolyethers are shown in Fig. 3 and the related data are summarized in Table 2. The width of the peaks is associated with the presence of unresolved vibronic structure and other inhomogeneous broadening. The absorptions around 380–410 nm are arisen from strongly allowed $\pi-\pi^*$ transition from the emitting segments in **P2** and **P3**, i.e. distyrylbenzene for **P2**, and distyrylstilbene for **P3**. However, in solution **P1** shows absorption peaks at 319 and 377 nm, whereas **O1** shows only one peak at 306 nm. Therefore, the absorption of **P1** at 377 nm should arise from $n-\pi^*$ transitions of the two aromatic oxadiazoles linked in sequence. Because of the electron-donating effect of extra hexyloxy groups in **P2**, its absorption maximum (403 nm) is somewhat displaced to a lower energy relative to **O2** (376 nm) and **P3** (392 nm). Moreover, the peaks at about 320 nm is also ascribed to $n-\pi^*$ transitions as that of **O1** at 306 nm. In film state, the absorption peaks of **P2** and **P3** appear at 413 and 379 nm, respectively, while that of **O2** locates at 362 nm [22]. Incorporation of hexyloxy groups in **P2** leads to about 50 nm red-shift compared to **O2**. However, extending conjugation length by one phenylenevinylene unit in **P3** only results in 17 nm red-shift compared to **O2**.

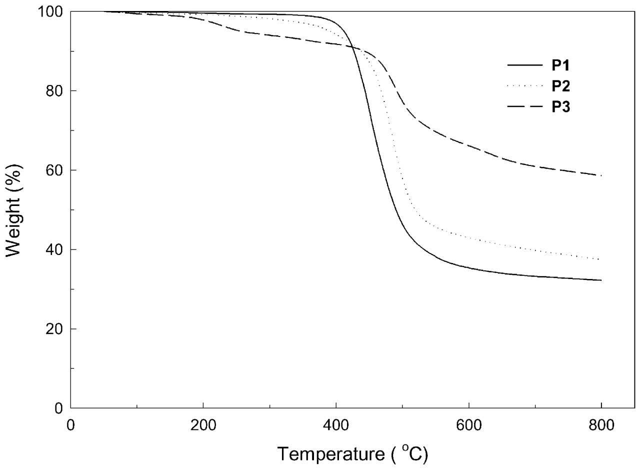


Fig. 2. Thermogravimetric curves of **P1**, **P2** and **P3** with a heating rate of 20 °C/min in nitrogen.

In film state, **P1** exhibits main PL maximum at 442 nm with a small peak at about 550 nm. The former can be attributed to the fluorescence of the two oxadiazole linked in sequence. Unfortunately, the origins of the latter have not been elucidated so far. The PL maxima of **P2** and **P3** in film state locate at 540 and 528 nm, respectively, indicating that they are green-emitting materials. The bathochromic shifts of **P2** and **P3** are about 65 and 53 nm, respectively, as compared to **O2** (475 nm). Therefore, in tuning the emitting

Table 2
Absorption and PL maxima of the copolyethers in solution and as films

Polymer	Solvent	$UV_{(soln)}$ (nm)	$UV_{(film)}$ (nm)	$PL_{(soln)}$ (nm)	$PL_{(film)}$ (nm)	Stokes shift[a] (nm)
P1	$C_2H_2Cl_4$	319, 377	326, 384	414, 430, 546	442, 551	58
O1	$CHCl_3$	306	305	–	382, 396	77
P2	$CHCl_3$	325, 403	325, 413	457, 488	540	127
O2	NMP	376	362	450	475	113
P3	$CF_3COOH/CHCl_3$ (1:3)	326, 392	324, 379	456	499, 528	149

[a] Stokes shift = $PL_{(film)}$ (nm) − $UV_{(film)}$ (nm).

color of isolated PPV-based segment, both side alkoxy attachment and resonance extension are effective strategies. However, two alkoxy groups seem more effective than one phenylenevinylene unit. In solution, the PL maxima of **P2**, **P3**, and **O2** are 488, 456, and 450 nm, respectively, indicating blue-shifts of 52, 72, and 25 nm as compared to those in film state. In general, the PL maxima exhibit red-shift in solid state due to aggregation interactions, which lacks in dilute solution. The Stokes shifts of **P2** and **P3** are greater than 120 nm, so the self-absorption effect would be small when fabricated as LED devices.

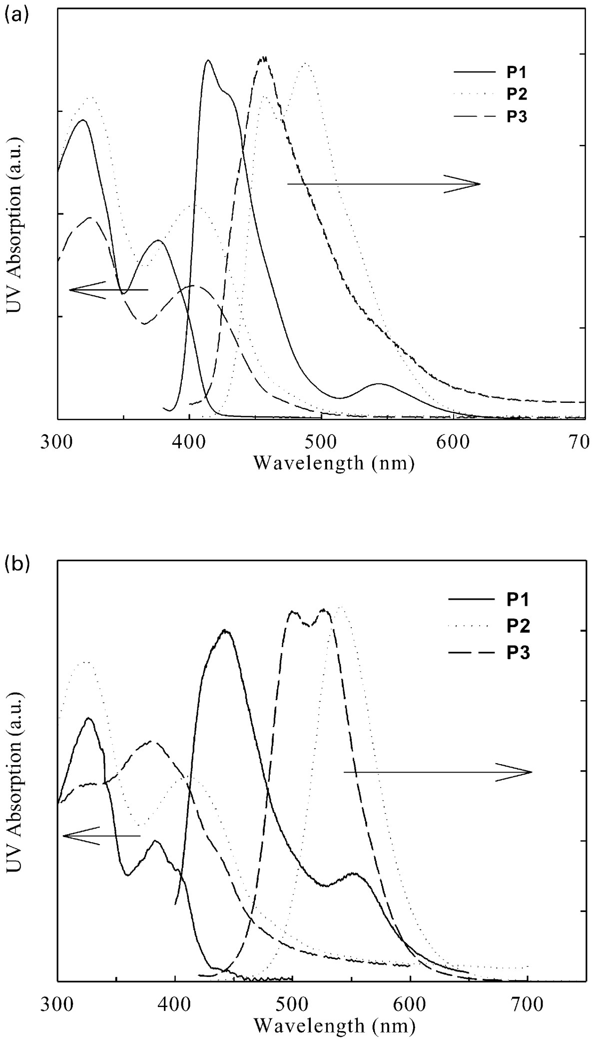


Fig. 3. Absorption and PL spectra of **P1**–**P3** (a) in solution, and (b) in film state.

3.4. Electrochemical properties

The ionization potential (IP) and electron affinity (EA) are important parameters in evaluating the redox property of luminescent polymers. Table 3 summarizes electrochemical parameters calculated from CV and band gaps (E_g^{opt}) estimated from onset absorption (λ_{onset}). The HOMOs (IPs) of **P2**, **P3**, and **O2** are 4.95, 5.22, and 5.23 eV, respectively, while the LUMOs (EAs) are 2.38, 2.60, and 2.39 eV. The band structures of the copolyethers are shown in Fig. 4. Extending one oxadiazole in **P1** (EA: 2.69 eV) results in significant increase in its EA as compared with **O1** (EA: 1.97 eV). Therefore, the LUMO levels are mainly controlled by the number of aromatic 1,3,4-oxadiazole groups. Incorporating hexyloxy groups in **P2** tend to decrease its IP value (4.95 eV) as compared with **O2** (5.23 eV). However, the LUMO of **P2** (2.38 eV) is almost the same as **O2** (2.39 eV). Accordingly, hexyloxy groups in distyrylbenzene unit raise mainly the HOMO levels of the copolyethers. The LUMO level of **P3** (2.60 eV) is lower than that of **O2** (2.39 eV), indicating that extended conjugation increases the EA.

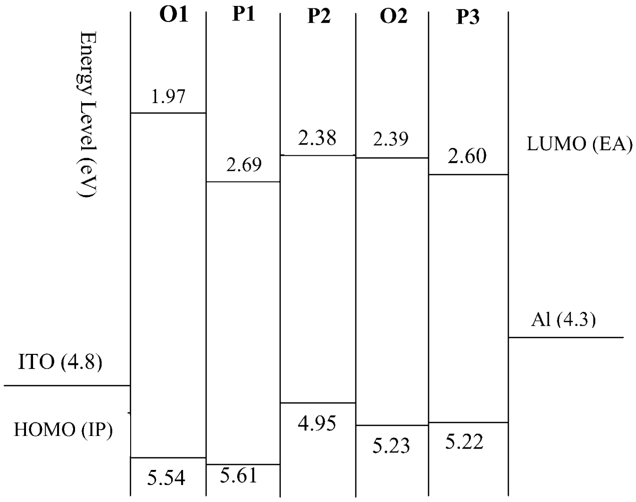


Fig. 4. Band diagrams of the copolyethers as estimated from the CV and absorption spectra.

Table 3
Optical and electrochemical properties of the copolyethers

Polymer	$E_{\text{onset(ox)}}$ vs. Ag/AgCl (V)	E_g^{opt} (eV)	$E_{\text{onset(ox)}}{}^a$ vs. E_{FOC} (V)	HOMO (IP)^b (eV)	LUMO (EA)^c (eV)
P1	1.28	2.92	0.81	5.61	2.69
O1	1.21	3.57	0.74	5.54	1.97
P2	0.62	2.57	0.15	4.95	2.38
O2	0.90	2.84	0.43	5.23	2.39
P3	0.89	2.62	0.42	5.22	2.60

[a] $E_{\text{FOC}} = 0.47$ V vs. Ag/AgCl.
[b] IP determined from the onset oxidation potential.
[c] EA determined from EA = IP − E_g^{opt}.

3.5. Single layer LED device

In order to evaluate the performance of these copolyethers, **P2** with good solubility was fabricated as single layer LED device with ITO as anode and aluminum as cathode. The thickness of **P2** was about 40 nm as determined from atomic force microscopic observation. As shown in Fig. 5, the threshold voltage was about 17 V and the luminance was 950 cd/m^2 at 26 V bias. At 20 V bias, the current density and luminance were 12 mA/cm^2 and 55 cd/m^2, respectively, with a luminance efficiency of 0.46 cd/A. This luminance efficiency is very high compared to 0.012 cd/A of MEH–PPV [24]. This can be attributed to the incorporation of isolated electron-transporting oxadiazole groups in backbone.

4. Conclusion

We have successfully prepared and characterized new copolyethers with isolated alternate emitting stilbene (**P1**), distyrylbenzene (**P2**) or distyrylstilbene (**P3**) chromophores and electron-transporting aromatic 1,3,4-oxadiazole groups in the main chain. Incorporation of hexyloxy groups in distyrylbenzene groups not only improves the solubility of **P2** but also leads to effective bathochromic shift in PL maxima (540 nm compared to 475 nm of **O2** without hexyloxy substitution). The tuning of luminescent color, such as **P3** (528 nm), can also be obtained by extending the resonance range of the emitting segment. The Stokes shifts of **P2** and **P3** are greater than 120 nm, so the self-absorption effect would be small when fabricated as LED devices. The band gap of **P1** (2.92 eV) and **P2** (2.57 eV) are narrower than **O1** (3.57 eV) and **O2** (2.84 eV), respectively. Their HOMOs and LUMOs are mainly determined by the emitting distyrylbenzene or distyrylstilbene chromophores and aromatic 1,3,4-oxadiazole groups, respectively. The threshold voltage and luminance of single layer ITO/**P2**/Al device are 17 V and 950 cd/m^2, respectively. The luminance efficiency of **P2** is 0.46 cd/A, which is greater than MEH–PPV (0.012 cd/A).

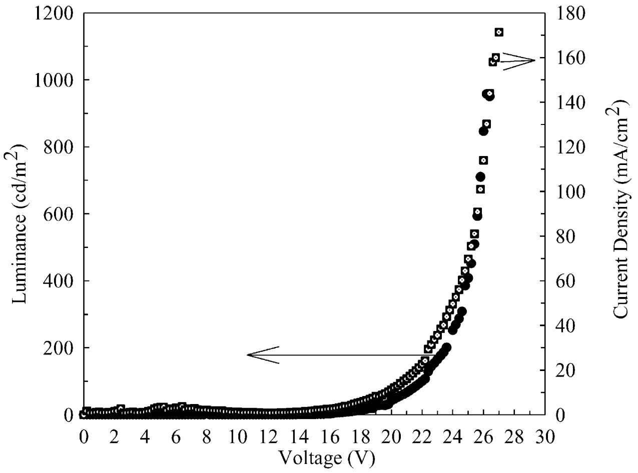


Fig. 5. Current density (□)–voltage-luminance (•) characteristics of ITO/**P2**/Al device.

Acknowledgments

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